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DESIGN AND OPERATING PARAMETERS FOR EMISSION CONTROL STUDIES: ASARCO, TACOMA, COPPER SMELTER

I. J. Weisenberg, et al

Pacific Environmental Services,
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16. ABSTRACT The report gives background design data for a specific copper smelter. The data is sufficiently detailed to allow air pollution control system engineering studies to be conducted These studies will be concerned primarily with lean SO2 streams that currently are not being captured. Physical layout of the smelter and the surrounding area is presented, along with existing control equipment. Ductwork that would be considered for future system tie-in is defined. Emissions from operating equipment, gas flow rates, temperatures, sulfur balance, and a process flow sheet are included. Utilities, stack dimensions, footing requirements, and solid waste handling are defined. Available area for new control equipment, gas characteristic variation, and potential new control equipment installation problems are discussed.

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DESIGN AND OPERATING PARAMETERS FOR EMISSION CONTROL STUDIES: ASARCO, TACOMA, COPPER SMELTER

by

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THE FIGURES IN THIS DOCUMENT ARE NONREPRODUCIBLE

THEREFORE ARE EXCLUDED FROM THIS REPORT.

A. INTRODUCTION AND SUMMARY

The purpose of this report is to present background design data on the ASARCO Incorporated Smelter at Tacoma, Washington in sufficient detail to allow air pollution control system engineering studies to be conducted. These studies are primarily concerned with lean SO_2 streams that are currently not being captured.

Physical layout of the smelter and surrounding area along with existing smelter and control equipment is presented. Ductwork that would be considered for future system tie-in is defined. Emissions from operating equipment, gas flow rates, temperatures, sulfur balance and process flow sheet are included. Utilities, stack dimensions, footing requirements, and solid waste handling are defined. Available area for new control equipment, gas characteristic variation and potential new control equipment installation problems are discussed.

The major uncontrolled sources of SO_2 at this smelter are the reverberatory furnaces and the roasters. Available space for installation of new equipment is limited. A DMA SO_2 concentration system producing liquid SO_2 and a sulfuric acid plant are used to control SO_2 from converter off gas.

B. PLANT LOCATION, ACCESS AND OVERALL GENERAL ARRANGEMENT

The ASARCO Smelter is located at the edge of Puget Sound in the towns of Tacoma, and Ruston, Washington. An enlargement of the USGS map, showing land contours of the immediate area is presented in Figure 1. Design altitude for the plant is sea level with latitude 47^{o} 18' and longitude 122^{o} 30'.

Overall plant view is shown as an artist's sketch in Figure 2. Smelter general arrangement is shown in Figure 3. A schematic showing relative location of the major emitting

KING CO.
PIERCE CO.
Point Dalco
Tahlequah
Neill Point
SCALE 1:24000
CITY BOUNDARY
DALCO PASSAGE
DALCO PASSAGE
POINT DEFIANCE PARK
Fort Nisqually
Salmon Beach
Point Defiance School
Holy Cross Sch
TACOMA
NARROWS
Point Evans
PACIFIC AVE
TACOMA AVE
NORTH 30TH ST
NORTH 37TH ST
10
14
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22
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24
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28
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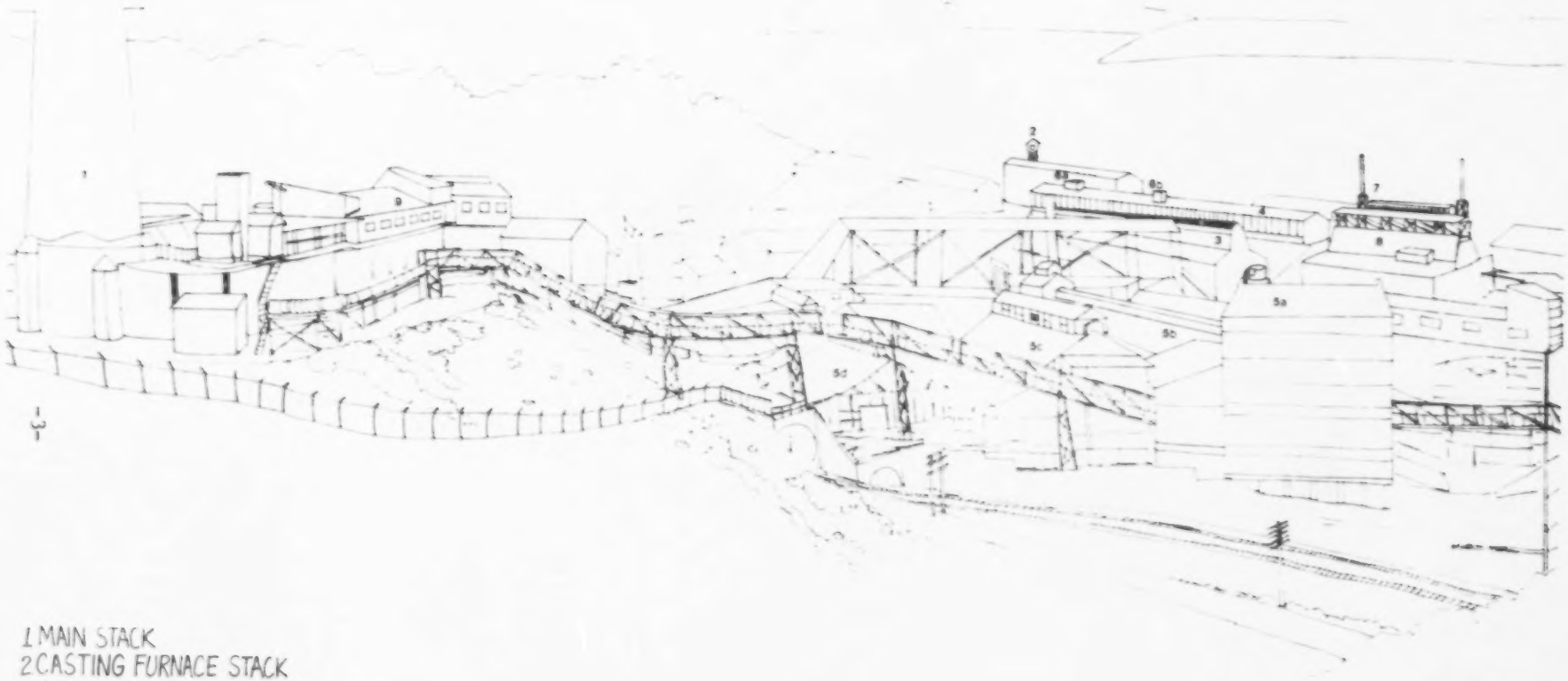
Figure 1

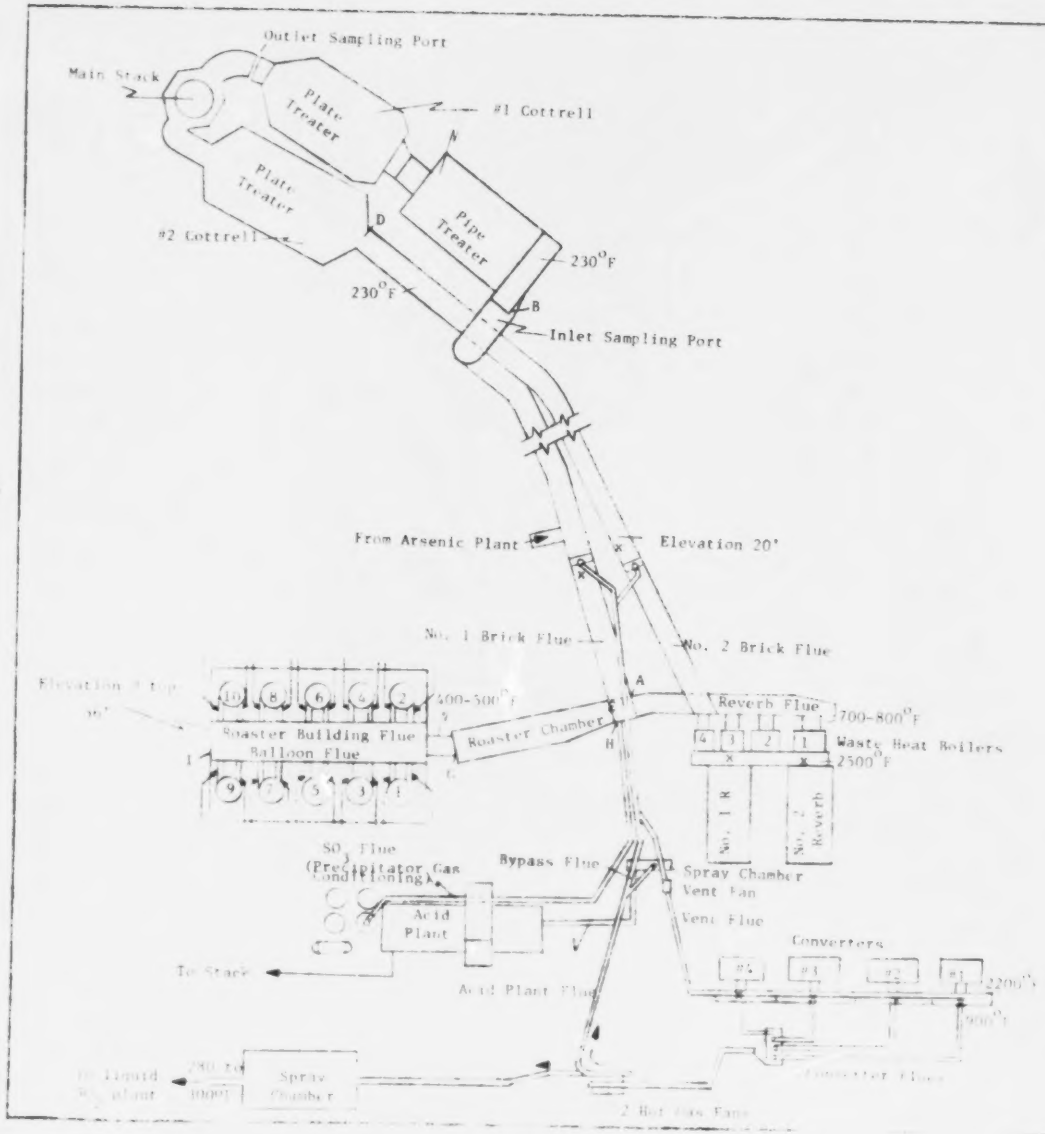
ASARCO TACOMA PLANT



1 MAIN STACK
2 CASTING FURNACE STACK
3 REVERBERATORY FURNACE
4 CONVERTOR BUILDING
5a ARSENIC PLANT b ARSENIC ROASTERS c ARSENIC KITCHENS d METALLIC ARSENIC PLANT
6a NORTH ANODE STACK b SOUTH ANODE STACK
7 ELECTROLYTE PURIFICATION PLANT
8. ROASTER BUILDING
9. ELECTROSTATIC PRECIPITATOR

Figure 2

Figure 3. SMELTER GENERAL ARRANGEMENT
(Located in Pocket Inside of Back Cover)



FLUE DIMENSIONS

Flue	L	H	W
No. 1 Brick Flue (A-B)	450'	24'	20'
No. 2 Brick Flue (C-D)	550'	24'	20'
Junction Tower (E)	26'	43'-4"	18'
Reverb Flue (G-H)	165-10"	20'-6"	27'
Roaster Building Flue (I-J)	120'	12'	12'-1"

Note: Roasters 1-6 10,000 SCFM/Roaster
Roaster 7-10 15,000 SCFM/Roaster

x Denotes Water Sprays

GAS SYSTEM DUCTWORK

ASARCO / Tacoma Branch | prepared July, 1975

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Figure 4

equipment with connecting duct work is given in Figure 4. The primary particulate emission sources are the crushing and screening operations, the roasters, the reverberatory furnaces and converters. The primary sources of sulfur dioxide are the roasters, reverberatory furnaces and the converters.

This plant, from a system and equipment standpoint, is one of the most complicated copper smelters in the United States. It not only includes the conventional copper roasters, reverberatory furnaces and converters, but also additional arsenic ore processing equipment and sulfuric acid plant and a liquid SO_2 plant for SO_2 control and other refinery equipment for producing nickel sulfate, dore and sodium selenite products. There are ten multi-hearth roasters, two reverberatory furnaces, four converters, and arsenic trioxide and a metallic arsenic plant.

The smelter portion of the plant consists of the coarse ore and concentrate handling and crushing equipment, ten Herreshoff roasters, two reverberatory furnaces, four converters, and three anode furnaces. Arsenic processing equipment consists of six Godfrey roasters (four usable), arsenic trioxide settling kitchens, arsenic trioxide storage and a metallic arsenic plant. This smelter has extensive varied equipment, primarily to handle a wide range of ore types since it is a custom smelter.

The pollution control equipment consists of five cyclones for the ore handling equipment along with coolers, spray chambers and precipitators for conditioning the converter and roaster gases going to the sulfuric acid plant and the liquid SO_2 plant. All tail gases from the acid plant and liquid SO_2 plant go to the stack.

The gases from the roasters and reverberatory furnace pass through electrostatic precipitators before going to the main stack.

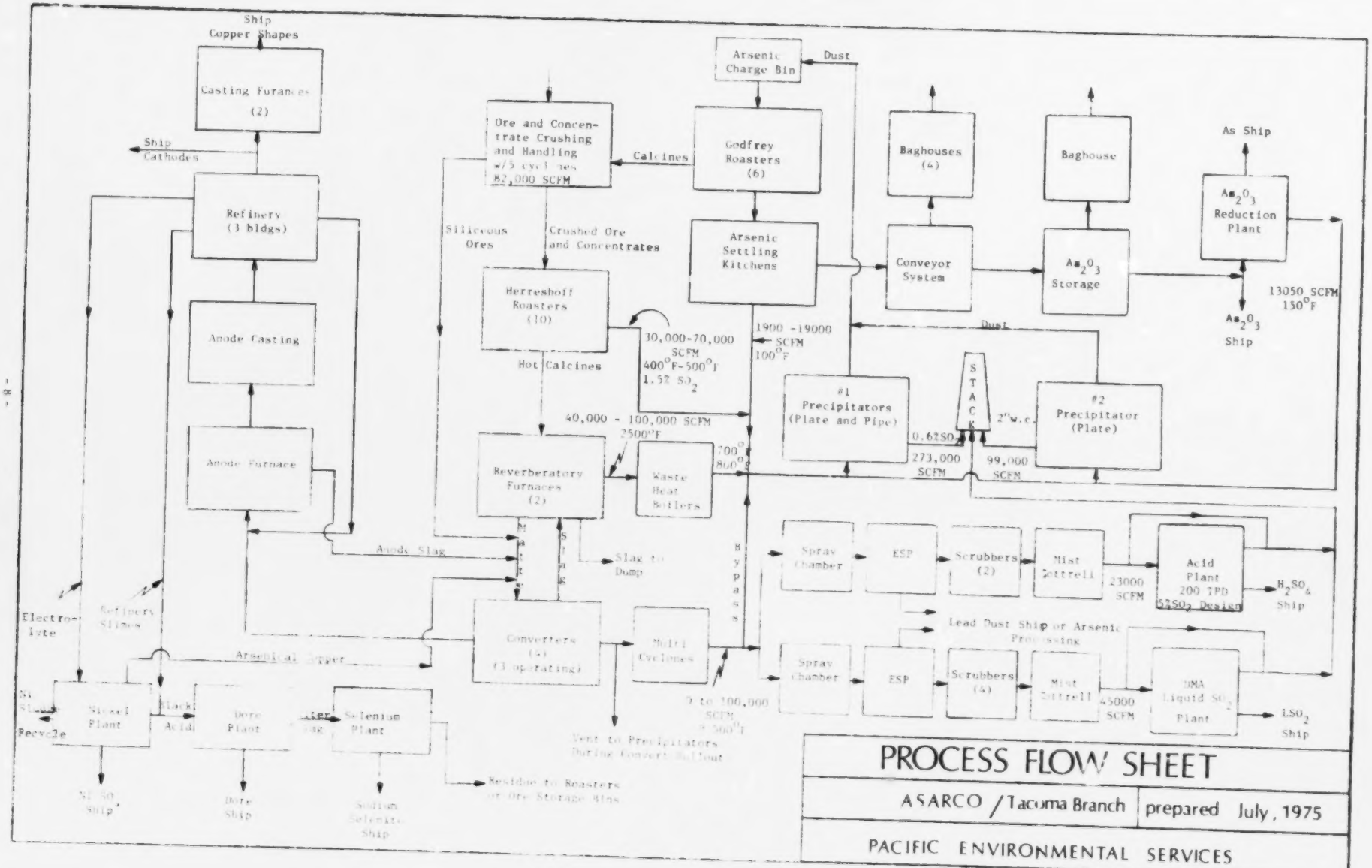
Figure 3 showing the overall plant arrangement indicates that there is relatively little available area for installation of control equipment. There is a possibility of the use of the Tacoma Tide Lands area on the easterly side of the smelter, and some smaller areas adjacent to existing equipment. The 50' x 100' nickel plant will be torn down in the near future and this site could also be used for new equipment installation.

C. PROCESS DESCRIPTION

The smelter flow sheet diagram is shown in Figure 5. The plant feed in the form of ore and concentrate goes to the Herreshoff multi-hearth roasters. Byproducts containing arsenic are fed to the Godfrey roasters. Analysis of the heavy metal and sulfur content of a typical roaster charge during a recent test period is shown in the following:

Date	Pb	Cu	As	Sb	Ni	S	Cd	Hg	Se
1/20/75	1.0	22.9	3.3	0.3	0.11	29.6	0.02	0.0051	0.024
1/21/75	1.0	23.7	3.8	0.4	0.04	30.0	0.02	0.0041	0.018
1/23/75	1.1	21.9	2.8	0.3	0.04	28.8	0.02	0.0038	0.015

The arsenical material after Godfrey roasting will pass as calcines to the fine ore bins for mixing and then to the Herreshoff multi-hearth roasters. The hot calcines from the multi-hearth are taken by larry car to one of two reverberatory furnaces where they are converted to matte containing 35-45% copper. The matte is then poured into ladles and taken by crane in the molten state to charge the converters. Slag from the furnace is sent to the dump.



PROCESS FLOW SHEET

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Figure 5

The converters produce a blister copper which is approximately 98-99% pure. This material is transferred by ladle in the molten state to the anode furnace where some minor impurities are removed by fire refining and the molten material cast into anodes. The anodes are then taken to the electrolytic refinery where they are reduced to electrolytic copper as cathodes or product copper. The electrolyte from the refinery is passed to the nickel plant which produces $NiSO_4$ for shipment, sludge which is recycled, and black acid which is sent to the dore' plant. Refinery slimes are sent to the dore' plant which produces dore' for shipment and niter slag that is sent to the selenium plant. Sodium selenide produced in the selenium plant is shipped and the plant residue is recycled.

The arsenic circuit consists of the arsenic charge bin which charges feed material to the Godfrey roasters for gasification of the arsenic material. The gasified arsenic material is then passed through the arsenic settling kitchens where the arsenic trioxide is condensed in the various sections. There are three arsenic kitchens, one ten chamber and two fifteen chamber baffled enclosures.

The nickel plant produces nickel sludge which is returned to the smelter and nickel sulfate which is shipped for further processing to other plants. Black acid is also produced and sent to the dore' plant. The dore' is shipped for further processing. Slag produced from the dore' plant is sent to the selenium plant which produces sodium selenite for shipment and residue which is passed back to the roasters or ore storage bins.

Gases from the multi-hearth roasters pass to an electrostatic precipitator and out the stack. Dust from this precipitator is recycled. Gases from the reverberatory furnaces are sent to an electrostatic precipitator and out the stack. Gases from the converters are sent either to a 200 TPD liquid SO_2 plant which produces liquid SO_2 or to a 200 TPD sulfuric acid plant. Gases from the converter are passed to a multicyclone before going to individual gas cleaning circuits for the liquid SO_2 or the sulfuric acid plants.

Offgases from the acid plant and the liquid SO_2 plant go directly to the stack. Converter gases can also be bypassed directly to the precipitator and then out the stack.

The gas cleaning circuit for each plant (the liquid SO_2 and sulfuric acid plants) consists of spray chambers, precipitators, scrubbers and mist precipitators to prepare the gases for either acid or liquid SO_2 production. Gases from the roasters or arsenic settling kitchens pass to precipitators and then out the stack. Gases from the reverberatory furnace pass through waste-heat boilers and then through precipitators and out the stack. Some of the gases from the converters during rollout are collected in the converter hoods and passed by a separate fan-blown system through the precipitators and then to the stack. Offgases from the acid plant and liquid SO_2 plant are passed directly to the stack.

Dust from the precipitators upstream of the liquid SO_2 and acid plants may contain lead which is shipped to a lead smelter for further processing.

Because of the nature of the ore received by this smelter from sources such as the Philippines, Arizona or other parts of the world, a wide range of products can be manufactured.

Nickel sulfate, dore', sodium selenite, copper cathodes, copper shapes sulfuric acid, arsenic trioxide, arsenic, lead dust, and liquid SO_2 can be produced.

Temperatures, volume flows and SO_2 percentage are shown on the flow sheet, Figure 5.

D. EMITTING EQUIPMENT

a. Multi-Hearth Roasters

There are ten Herreshoff multi-hearth roasters arranged in a double row as shown in Figure 4. Roaster hearth area is 1345 square feet with dimensions of 19 feet diameter by 25 feet high. The top

of the roasters is approximately 40 feet from ground level.

There are usually five roasters used at one time. However, there may be as many as six and as few as none in operation at any particular time. Dampers are located in the roaster uptake duct to isolate units not in operation. Roaster ore is heated to approximately 900°F.

As is normally encountered with multi-hearth roaster, considerable leakage is present throughout the associated ductwork as well as the units themselves. This results in dilution air entering the system and reducing the concentration of pollutants such as SO_2.

The capacity of each roaster is 1200 tons per day. Eight loads per hour is considered the normal production rate. One load weighs approximately 6.5 tons.

b. Reverberatory Furnaces

Two reverberatory furnaces of approximately 1200 TPD capacity each are installed. No. 1 has dimensions of 30' wide by 110' long and No. 2 has dimensions of 32' wide by 110' long. The draft for each furnace is generated by a steam turbine driven fan. Four Wagstaff guns are used to feed each furnace at the side.

Most of the time, only the No. 2 reverberatory furnace is used. Within the last two years No. 1 has only been used for a total time of two months.

A negative .02 inches of water pressure is maintained automatically in the reverberatory furnace during normal operation. During charging of the furnace the control damper is opened wide by manual overide to minimize pressure surges. The fuel supply is also cut off for a present time of approximately 30 to 40 seconds to minimize the occurrence of positive pressure.

Maximum fuel consumption for the reverberatory furnace is 180,000 CFH of 1030 BTU per cubic foot gas. An air to fuel ratio of 10 to 11 is used for furnace firing. There are three waste-heat boilers downstream of the two reverberatory furnaces, one on #1 and two on #2. Each of the #2 furnace boilers has a rating of 1000 horsepower and the #1 has a rating of 1890 horsepower. Gas temperature is reduced from 2500°F to 700°F - 800°F across the waste-heat boilers. Approximately 35 GPM of water is used in each boiler.

c. Converters

Three Peirce-Smith converters have dimensions of 13 feet diameter by 30 feet long and one Peirce-Smith converter 11 feet diameter by 26 feet long. Normally only three converters are used at any one time. Blowing is limited to no more than two at any one time and generally a finish blow on one only will be conducted.

Normal converter cycle takes 12 hours. Total converter operation seldom exceeds 40 hours per day and has a range of 25-40 hours per day. The blowing rate will vary from 17,000 SCFM to 25,000 SCFM. With dilution air the volume flow from each converter through the hood during the blowing periods is approximately 38,000 - 40,000 SCFM.

Sulfur dioxide of up to 10 percent has been measured immediately downstream of the converter opening at the hood. Average SO_2 percentages are in the 3-4 percent range.

d. Arsenic Circuit

The arsenic kitchens are rectangular shaped, brick or concrete ovenlike structures divided into 10 or 15 chambers. The gases are continuously passed at very low velocity through each chamber resulting in gradual cooling by radiation. The arsenic condenses at approximately 400°F and is collected in the intermediate chambers in the kitchens. The condensed arsenic trioxide is removed

periodically from the settling kitchens and placed in storage. This material is either shipped as is or reduced to metal in the arsenic trioxide reduction plant.

e. Other Emitting Equipment

Material handling in the feed preparation area during crushing or preparation operations generates particulates.

The anode furnace generates small quantities of SO_2 and particulates.

Leaks in ducts and at other pieces of equipment can generate SO_2 and particulates.

Ladles holding matte and slag will produce visible fugitive emissions. The liquid SO_2 plant and the acid plant will produce small quantities of SO_2 in the offgas.

Dust from the precipitator handling the reverberatory furnace and roaster gases is the major source of arsenic processed in the arsenic kitchens. The converter dust obtained from the precipitator handling the converter gases is also processed but since it has a lower percentage of arsenic this material is recycled through the arsenic roasters and then shipped to another plant for lead recovery. The converter dust is processed at separate times through the arsenic circuit. The arsenic in the charge is eliminated 20% from the roasters, 60% from the reverberatory furnace, 10% out of the matte and 10% out of the reverberatory slag.

E. EXISTING CONTROL EQUIPMENT

The coarse ores and concentrate handling and crushing area has five cyclones for particulate collection.

Three electrostatic precipitators are used for brick flues No. 1 and No. 2 to collect particulate before the gases from all collection points in the smelter pass out the single main stack. Since the two main brick flues join together and automatically balance the flow, there is no complete separation between roaster and

reverberatory furnace offgases. However, the two precipitators in brick flue No. 1 (Fig. 4) generally treat the roaster offgases and the single precipitator in brick flue No. 2 treats the reverberatory furnace offgases. There is no SO_2 collection for the roaster or reverberatory furnace offgases. Water and sulfuric acid are sprayed into the flues upstream of the precipitators for conditioning and cooling. The gases that join at the roaster chamber and reverberatory flue are conditioned for precipitation by adding small quantities of SO_3 taken from the acid plant.

The precipitator in brick flue No. 2 consists of five sections with six units in each section. The overall dimensions are 7'9" x 14' 0" x 72'0". The upstream pipe precipitator in brick flue No. 1 has two sections of 4-1/2 units each consisting of 84 - 12" x 15' x 0" pipes per unit. The downstream precipitator in brick flue No. 1 is a plate-type of five sections, each section having four units each 8'6" wide x 7'6" long x 12'0" high. The precipitators are designed to handle a total volume flow of 345,000 ACFM.

The single contact acid plant was originally designed in 1950 for 100 TPD at 3% SO_2. It has been enlarged to the 200 TPD capacity at 5% SO_2 and is capable of handling 23,000 SCFM.

Acid production record in tons:

Year	Tons H_2SO_4
1969	38,379
1970	37,485
1971	40,154
1972 (first half)	22,230

The acid plant precipitator is designed to handle a volume flow of 34,000 ACFM.

The liquid SO_2 plant processes up to 45,000 SCFM of the converter gases. This system uses dimethylaniline (DMA) for absorbing the gaseous SO_2 and then regenerating by stripping with steam. The concentrated SO_2 is produced as a 100% gas. It is liquified by compression and is then stored under pressure. A description of the DMA process is included in Appendix A.

The DMA concentration plant contains 20,000 gallons of DMA which is passed between the pregnant tank and the stripped tank. When there is no SO_2 being generated by the converters, the system operation can be cut back so that very little DMA is processed.

Some of the liquid SO_2 is shipped to the east coast under a contractual agreement that ASARCO has with a chemical firm. This long shipping distance results in a net cost to ASARCO for SO_2 production. The price of SO_2 must be competitive with that produced from elemental sulfur burning.

F. GAS SYSTEM DUCTWORK

A plan view of the interconnecting ductwork between the roasters, reverberatory furnaces, converters, acid plant, liquid SO_2 plant and the stack is shown in Figure 4. Gases from any one of ten multi-hearth roasters pass into the roaster building flue, then to the roaster chamber or settling flue and then to the junction with the reverberatory furnace flue. Gases from the reverberatory furnaces pass through waste-heat boilers, then to the reverberatory furnace flue. The No. 1 brick flue takes most of the gases from the roaster building and No. 2 brick flue takes most of the gases from the reverberatory furnaces. However a crossover link is installed to allow system pressure balance. The draft is obtained from the 563 foot high main stack and is 2" W.C. at the base. Duct dimensions are shown in Figure 4. Gases from the converter hoods are drawn by two hot gas fans and allowed to pass either to the liquid SO_2 plant, the sulfuric acid plant or to the stack. An additional line is used to provide SO_3 from the acid plant to condition the gases for the final precipitator treatment.

A separate vent system connected to the converter hoods, is used during converter rollout to minimize fugitive emissions during the non-blowing phase. Not all gases enter the hood during this phase because of geometrical considerations. The duct is connected to the brick flues which pass this gas out the tall stack.

Elevations of principal ductwork are as follows: (All elevations are to the bottom of the flue).

No. 1 Brick Flue	67' - 150'
No. 2 Brick Flue	67' - 150'
Roaster Chamber Flue	54'
Roaster Building Balloon Flue	65'
Reverberatory	50'

The acid plant and SO_2 plant offgases are vented to the main stack downstream of the precipitators.

G. SULFUR BALANCE AND GAS COMPOSITION AT SYSTEM EXIT

Typical Sulfur Balance Data - TPD Sulfur

From ore concentrates charged	270
To 100% sulfuric acid produced	39
To liquid SO_2 produced	71
To slag	6
To other waste (not emissions)	2
To SO_2 emissions	152

The above are recent typical data based on monthly measurements, Reference 2. Table 1 summarizes representative sulfur balance by emitting equipment.

SO_2 concentration at the outlet of the multi-hearth roasters was measured to be 1.5% with 3.5% to 5.0% water. SO_2 concentration at the outlet of the precipitators in brick flue No. 1 was 0.6%, Reference 3.

TABLE 1

ASARCO/TACOMA

AVERAGE SULFUR BALANCE SUMMARY

Sulfur Input	Roasters (Uncontrolled)		Reverberatory Furnaces (Uncontrolled)		Converters (Partially Controlled)		Slag and Solid Waste (Controlled)	Fugitive Emissions (Uncontrolled)	Sulfur Captured (Slag and Acid Plant)
TPD-S	$\%SO_2$	TPD-S	$\%SO_2$	TPD-S	$\%SO_2$	TPD-S	TPD-S	TPD-S	TPD-S
300	1.5	60	1.0	84	3 to 4 (up to 10%)	141.6	4.8	9.6 (By difference)	158.4

Suspended particulate in tons per year, and SO_x in tons per year for the years 1971-1975 are shown on Table 2, Reference 4.

Low level sources near the plant that have had some control are listed in the following Table 3 (Reference 6). Dates show the date of control.

Figure 6 and Figure 7 show mass distribution of particles upstream and downstream of the precipitator in brick flue No. 1 which carries most of the gases from the roasters. As can be seen, the precipitator takes out a major portion of the .1μ to 10μ material but does not effect the less than .1μ particles to as great an extent. Mass mean diameter at the precipitator outlet has been determined to be .12 μ , std. dev. .162 μ (Reference 6).

Particulate emissions from the tall stack (from all plant equipment) are estimated by PSAPCA and ASARCO as follows:

	Total Part. T/Y	AS_2O_3 T/Y	Material T/Y Under 3.2μ (Reference 6)	AS_2O_3 T/Y Under 3.2μ (Reference 6)
ESP ASARCO (Estimate)	150	80	99	52 (3)
PSAPCA (Estimate)	191	102	140	72 (3)

The chart, Figure 8, shows the sulfur captured by month during 1974 and 1975 from the converter gases related to sulfur input in the matte. This shows the relative sulfur captured in the slag, liquid SO_2 and sulfuric acid and indicates the major improvement obtained with the liquid SO_2 plant.

H. GAS CHARACTERISTIC VARIATION

The SO_2 concentrations in the offgas from the reverberatory furnace will vary significantly depending upon the charge rate and the various sulfide materials contained in the charge. The normal

JMR 4-14-75

Table 2

TACOMA SMELTER EMISSIONS ESTIMATES

SUSPENDED PARTICULATE TONS/YR							SO_x TONS/YR	
YR.	TALL STACK			LOW LEVEL			TALL STACK	LOW LEVEL
	ARSENIC TRIOXIDE	CADMIUM	TOTAL	As_2O_3	CADMIUM	TOTAL		
1971	506	3.4	970	296+	2.0+	1285+	164,600	6814
1972	228	1.6	438	281+	1.9+	1218+	156,000	6460
1973	176	1.2	335	266+	1.8+	1145+	148,000	6127
1974	164	0.6	308	167+	1.5+	967+	117,900	3414
*1975	80	0.2	150	90.+	.98+	682+	99,600	3400

+ INDICATES THAT THERE ARE LOW LEVEL EMISSIONS WHICH HAVE NOT BEEN MEASURED OR ESTIMATED.
* 1975 ESTIMATE BASED ON ASARCO REPORTS FOR JANUARY AND FEBRUARY.

Reference 6

	TABLE 3. LOW LEVEL EMISSION SOURCES AND CONTROL TECHNIQUES	Date of Control
1.	Wind Blow Dust from ASARCO Property	6/73
2.	In-Plant Road Dust	6/73
3.	Improve Matte Ladle Loading Hood	2/74
4.	Arsenic Storage and Loadout	2/74
5.	Dust from Converter Flue Unloading	3/74
6.	Conveyor for Arsenic Feed Plant	4/74
7.	Larry Car Covers	11/74
8.	Reverb. Furnace Slag Launder	5/75
9.	Reverb. Furnace Charge Guns	2/75
10.	Flue Dust Handling	5/75
11.	Converter Fugitive Emissions	
12.	Ore Roasters Fugitive Emissions	
13.	Slag Dumping	
14.	Gravel Roads Outside Plant	7/75
15.	Wind Blown Dust Outside Plant	7/75
16.	Sealing Arsenic Building	
17.	Anode Furnaces	
18.	Reverb. Furnace Slag Launder for Converter	4/76
19.	Minimum Blow on Converters	12/75
20.	TallStack	
21.	Metallic Arsenic Plant	
22.	Original Cottrells (ESP)	1917
23.	Acid Plant	1950
24.	New ESP Rappers	12/71
25.	New ESP Voltage Regulators	12/73
26.	Use of SO_3 for ESP Dust Conditioning	7/74
27.	Liquid SO_2 Plant	7/74
28.	Roaster SO_2 Control	
29.	Baghouse for Arsenic Plant Flue	
30.	Ventillation As Pulling for Kitchens	

Figure 6

Mass distribution of particles upstream of the #1 electrostatic precipitator (assuming particle specific gravity = 3.865).

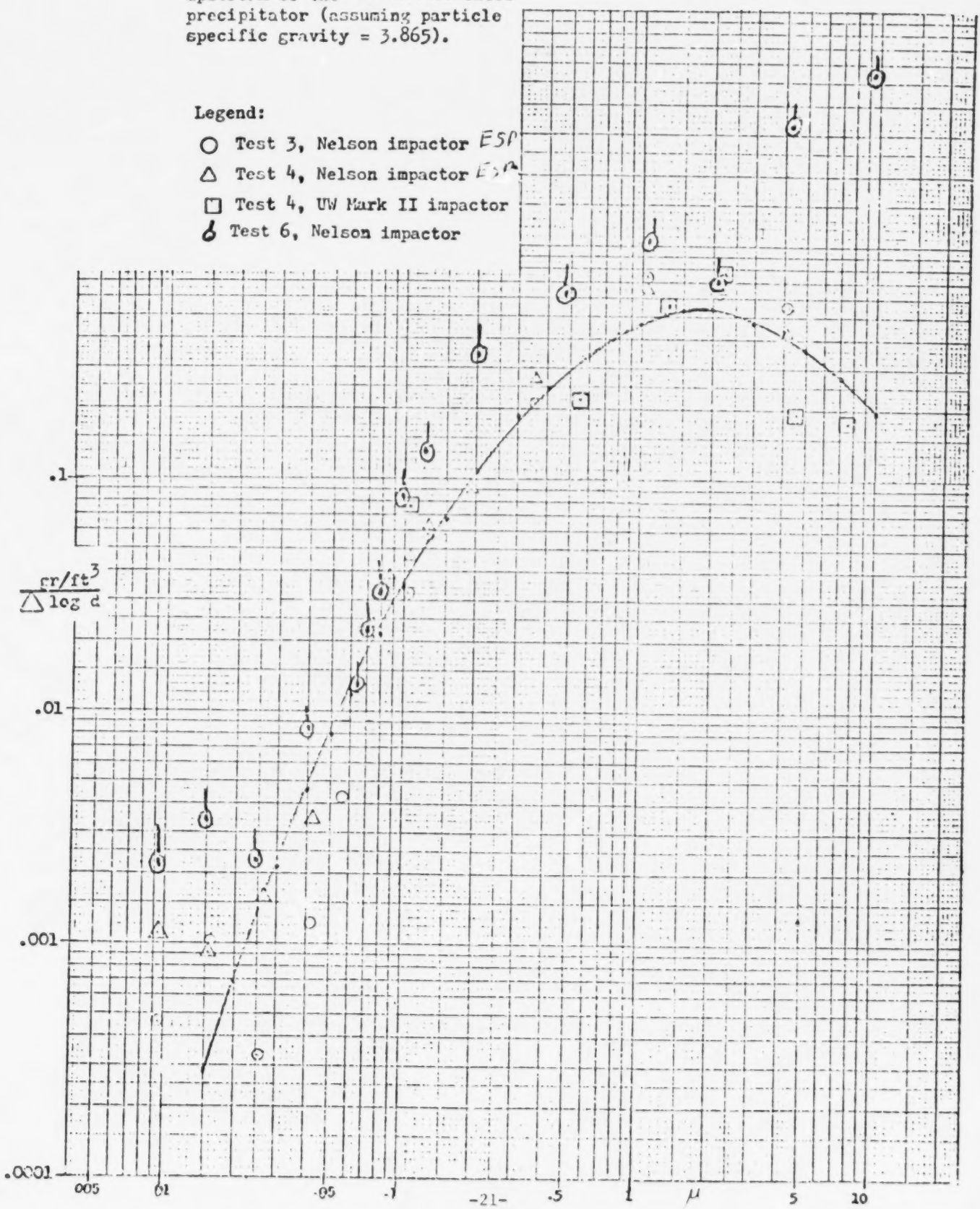


Figure 7

Mass distribution of particles downstream of the #1 electrostatic precipitator (assuming particle specific gravity = 3.865)

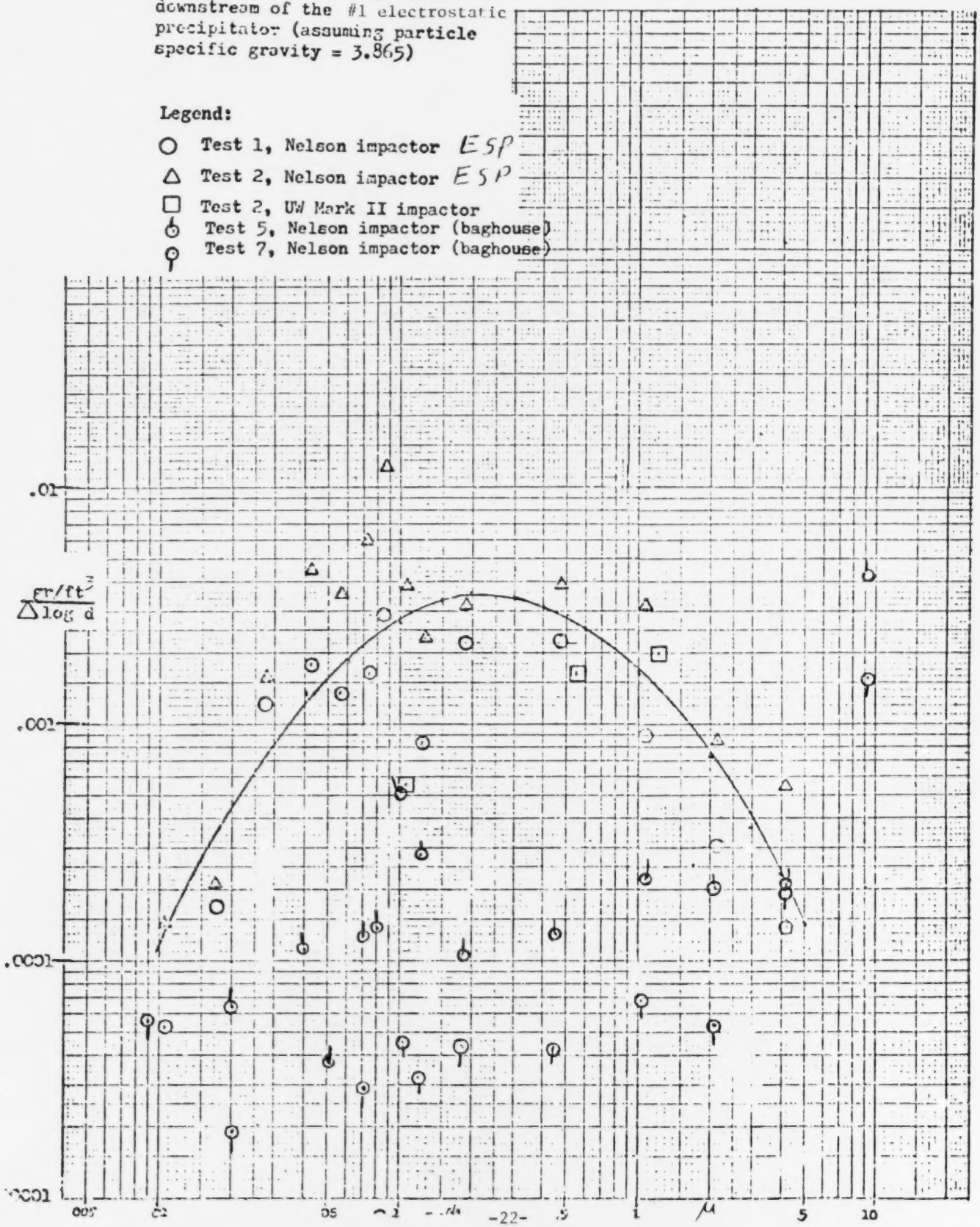
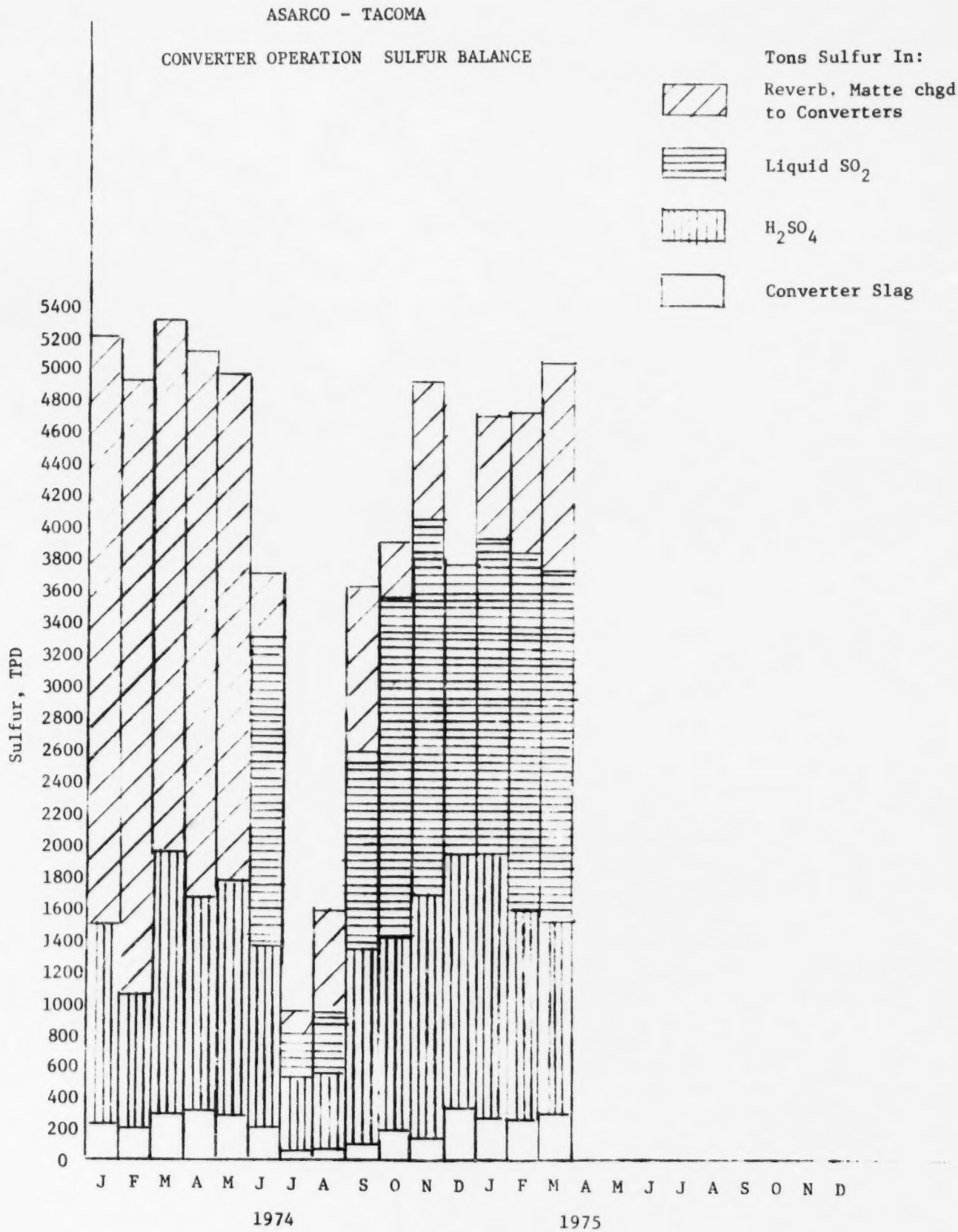


Figure 8


ASARCO - TACOMA
CONVERTER OPERATION SULFUR BALANCE
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Reverb. Matte chgd. to Converters
Liquid SO_2
H_2SO_4
Converter Slag
Sulfur, TPD
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or average charge rate into the furnace is four loads per hour. However, this can vary between two and eight loads per hour. This variation is a result of intermittent pollution control and smelter operations and can be controlled only to a limited extent. Table 4 shows the effect of variation in charge or dropping rate into the furnace on the percent SO_2 concentration in the offgas. These measurements (Reference 5) were taken primarily in the steel flue immediately downstream of the No. 2 reverberatory furnace. The firing rate will also have an affect on the percent SO_2. Table 5 shows a variation from .16% SO_2 up to 1.52% SO_2. This occurred over a volume flow range of 33,338 SCFM to 54,600 SCFM.

Table 5 further shows the potential variation in SO_2 concentration. For the date of 2/16/70 the average percent SO_2 between drops was 1.0%. This occurred at a charging rate of 6 loads per hour. Maximum peak percent SO_2 during this same period was measured as 13.0% but there is considerable question as to the accuracy of this number. The average of peak values for this same period (1 hour) was 6.5%. Thus, it can be seen that between at least 1.0% and 6.5% can be encountered over a relatively short period of time. The second set of data in Table 5 had a charging rate of 8 loads per hour and indicates less of a variation but still shows a peak of 5.0% to an average between drops at .75%.

From these data it can be said that peak SO_2 may vary between 7-13 times the average percent SO_2. Any control system must be designed with this variability in mind.

SO_2 concentration in the converter offgas also varies considerably because of the batch nature of the operation. Also, the variation in actual metallurgical operation between slag blows and copper blows will cause a variation in percent SO_2. Between blows the converter may be rolled out for slag pouring or material charging. When the converter is not blowing the hood above the converter collects the gases and passes them to a separate vent system. See Figure 4.

Table 4.

45-Minute Sampling (3 Drops)

Date	Dropping Rate Loads/Hour	% SO_2 Shell	% SO_2 Reich	Volume Std. cfm	Tons S Elim./Hr.	Sample Location
/21/70	8		1.07	-	-	#2 Reverb. Uptake (Upstrm. W.H.B.)
/22	7		0.16	-	-	#2 Reverb. Steel Flue (Dwnstrm. W.H.B.)
/27	7		0.26	-	-	"
/13	5		0.49	-	-	"
/16	2		0.15	-	-	"
"	6		0.21	37,586	0.22	"
"	6		0.21	39,439	0.23	"
"	4		0.45	33,338	0.41	"
"	5		0.21	-	-	"
"	5		0.28	-	-	"
"	4		0.30	-	-	"
"	4		0.43	-	-	"
"	4		0.45	-	-	"
"	4		0.32	-	-	"
"	6	-	1.64	49,700	2.23	"
/12	5	1.09	1.21	54,600	1.81	"
/13	6	1.55	1.52	52,000	2.21	"
/13	6	0.82	1.40	48,700	1.87	"

Table 5.

Reverberatory Furnace Sulfur Elimination

As A Function of Charge Rate

Date	Dropping Rate Loads/Hour	% SO_2	Volume Std. cfm	Ton S Elim./Hr	Sampling Period*
2/16/70	6	1.0	51,300	1.41	Average between drops
"	6	13.0(?)	51,300	18.30	Max. Peak during drop
"	6	6.5	51,300	9.14	Average Peak during drop
9/10/71	8	0.75	51,000	1.04	Average between drops
"	8	5.0	51,000	6.98	Max. Peak during drop
"	8	4.0	51,000	5.59	Average Peak during drop

*Sampling was done in #2 Reverb. Steel Flue

The attempt is always made to maintain at least one converter blowing gases into the system at any given time. Usually a converter will be provided with 18,000 - 20,000 SCFM to the tuyeres. An additional 100-120% of dilution air is generally estimated to be added to this gas flow resulting in a total gas flow from each converter in the range of 35,000 - 40,000 SCFM. When a converter is blowing there will usually be approximately 38,000 SCFM and an SO_2 content in the range of 4.0 to 4.5%.

Because of the above, the gas volume flow from the converter line to the control system acid plant and liquid SO_2 plant can vary over a wide range from maximum to zero. Stored liquid SO_2 can be fed to the acid plant when the smelter is not generating a sufficient quantity, thereby allowing the acid plant to operate on a continuous basis to minimize startup inefficiencies and corrosion. Because of contractual commitments, ASARCO is generally not able to operate in this manner.

I. STACK DESCRIPTION

The 563-foot high stack has a top diameter of 24 feet. The top of the stack is located 713 feet above sea level.

Inlet temperature at the bottom of the stack is 185°F.

Stack construction is brick and mortar with an acid brick lining.

The acid plant and liquid SO_2 plant offgases are ducted to the main stack.

There is a preheater used to heat the gases going up the stack. When the preheater is not used a temperature of 150°F will be reached 200 feet up the stack. When the preheater is used, a temperature of 250°F is reached at the 200-foot elevation.

J. PRESENT TECHNIQUE FOR SOLID-WASTE HANDLING

Slag is sold for sandblasting, roof granules or portland cement aggregate. Dust taken from the dust collection devices are recycled. Lead containing dusts are shipped to the Helena, Montana smelter for processing. Dusts high in arsenic are processed through the arsenic circuit.

K. FOOTING AND STRUCTURAL REQUIREMENTS

Most of the smelter is constructed on fill slag and some sawmill wastes are the primary fill constituents. Pilings, installed by drilling and driving, are required on 3-foot centers. City of Tacoma local codes apply. Seismic zone 3, wind load 25 PSF, and snow load 15 PSF are used for design.

L. EXISTING AND POTENTIALLY AVAILABLE UTILITIES

There is an abundant water supply and it is expected that any new control equipment can be supplied with the existing system.

Future increases in gas usage as fuel are unacceptable due to the decreasing availability of natural gas. There are no additional loads that can be supplied to the gas system. Direct-fired and waste-heat boilers provide steam for compressed air, heating and SO_2 DMA stripping. The #1 furnace waste-heat boiler is rated at 1890 HP and 65,205 lb/hr of steam and the two #2 furnace waste-heat boilers are each rated at 1000 HP and 34,500 lb/hr of steam. Tacoma City Light Company provides electricity required. The available substation is now operating at approximately 75% capacity. There is an additional 5,000 KVA capacity available.

M. POTENTIAL NEW CONTROL EQUIPMENT INSTALLATION PROBLEMS

One of the major problems at this particular smelter would be to find space for additional control equipment near the emission source. The Tacoma Tide Lands area would appear to be the most logical for installation of any extensive control equipment. As can

be seen from Figure 3 the plant area is fairly well crowded with buildings, flues and equipment. The area adjacent to the street is also a potential space for control equipment, though it also is some distance from the major emission sources. The area along brick flue No. 1 adjacent to the metallic arsenic area is also a potential space for control equipment. The smelter is obtaining to obtain a permit to fill ten acres with slag up to the 1961 inner harbor line which could be used but at additional fill expense. The 50' x 100' nickel plant will be torn down in the near future making this site available for new equipment.

Tests with a pilot baghouse were performed to compare baghouse collection efficiency with electrostatic precipitator collection efficiency. The tests indicated that the baghouse was approximately 25 times better at collecting particles less than 1 micron.

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2. ASARCO sulfur balance, March 1975.
3. Puget Sound Air Pollution Control Agency data taken using Ritagawa tubes and Umgard pump.
4. ASARCO Data, 4-14-75.
5. ASARCO data.
6. Puget Sound Air Pollution Control Agency data and calculations.

ture combustion. In this case, a preheat of over 500° C. in gas would be necessary to maintain the required temperature le reduction furnace.

Asarco was considering the installation of a commercial 35-ton-day sulfur unit at Garfield in 1944. By that time, however, household requirements of Salt Lake City for natural gas dur- the winter months became so heavy that existing pipe lines ld not supply this demand and at the same time carry the strial load. The project was therefore shelved.

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LIQUID SULFUR DIOXIDE FROM WASTE SMELTER GASES

Use of Dimethylaniline as Absorbant

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This paper reviews the various pilot plant investigations conducted by the American Smelting and Refining Company during the past 30 years with the object of perfecting a process that could produce liquid sulfur dioxide commercially from waste smelter gases. Processes developed along these lines in Europe are briefly discussed and reasons given for the selection by American Smelting and Refining of anhydrous dimethylaniline as its preferred reagent. The novel features of process system and plant construction are described in detail by reference to the flow diagram of the 20-ton plant installed September 1947, in the company's lead smelter at Selby, Calif. The benefits of the improved system of operation, as compared with the procedure followed in European plants, are emphasized; among these are high purity of product and facility of operation. Basic data as indicated by 1949 operations at Selby are given, covering such items as reagents, steam, power, cooling water, labor, and supervision. The possibilities of the process' being applied to the recovery of sulfur dioxide from low-grade industrial gases by the use other reagents having a high absorptive capacity for the gas are briefly noted.

THE American Smelting and Refining Company for the past 30 years, engaged in investigating various methods for recovering sulfur dioxide from waste smelter gases with the twofold objective minimizing smoke conditions and perfecting a process that could compete with limestone in the sulfite wood pulp industry. Over this period, pilot plants of from 1 to 15 tons' capacity have been operated, using the Haenisch-Schroeder water-absorption process with direct compression of low-grade converter gas in a ten-ton-per-day pilot plant (*6*), the ammonium sulfite-bisulfite cycle (*4*), the Lurgi "sulphidine" process using sulphidine in water suspension (*9*), and finally the Asarco process using dimethylaniline (*2, 3*). Laboratory experimental work was also conducted on other reagents, particularly Imperial Chemical basic aluminum sulfate (*1, 7*) and Lurgi's toluidine-in-water suspension (*9*).

The final choice of process lay between Lurgi's sulphidine in water suspension and absorption in anhydrous dimethylaniline. The latter was selected because it was simpler to operate and also because the process cycle of operation, patented by American Smelting and Refining Company, permitted material savings in reagent loss, steam consumption, and labor cost as compared with the Lurgi cycle as operated in Europe by Metallgesellschaft. The sulphidine system as developed by Metallgesellschaft consisted of separate units for absorption of sulfur dioxide, recovery of sulphidine vapor in acid scrubber solution, regeneration of the bisulfate with soda ash and cooling to 2° C., and desorption of sulfur dioxide. These various operations involved considerable reagent loss, excessive labor, and high steam consumption.

The principal novel features of the Asarco process using dimethylaniline reagent consist of:

1. Incorporating the regeneration unit for treatment of recaptured dimethylaniline sulfate as an integral part of the absorption-desorption cycle. This saves labor and steam and reduces the possible loss of reagent.
2. Limiting the absorption-desorption cycle and dimethylaniline recovery system to two main bubble-cap tray towers where all solutions and gases come in contact with lead only; this eliminates corrosion.
3. Installing just above the absorption section of tower, two bubble-cap trays where the sodium carbonate solution is converted to sodium sulfite or bisulfite by the residual sulfur dioxide in the exit gases; this permits regeneration of dimethylaniline in the closed absorption-desorption cycle, allowing the concentrated sulfur dioxide to enter the compressor free of carbon dioxide.
4. Recapturing practically all the dimethylaniline vapor, which has escaped from the absorption tower, in a bubble-cap, nine-tray extension of the same tower where the vapor is scrubbed with dilute sulfuric acid flowing countercurrent to gas flow.
5. Recovering and returning a considerable portion of the dimethylaniline to the absorber without the necessity of heating it in the main regeneration unit.

A comparison of dimethylaniline and xylidine, as absorbents for sulfur dioxide, shows that each has some advantages over the other. Dimethylaniline is used substantially dry whereas xylidine is used in a mixture of one-half xylidine and one-half water.

The ability of dimethylaniline and xylidine to absorb sulfur dioxide from flue gas is shown on Figure 1, curves *A* and *B*. The absorption isotherms show that xylidine, curve *B*, is a better absorbant for sulfur dioxide in the lower percentages by volume, and dimethylaniline, curve *A*, is a better absorbant for sulfur dioxide

31

in the latter concentrations. The two isotherms cross at about 3.5% sulfur dioxide by volume.

The solubility of sulfur dioxide from gas mixtures in dimethylaniline follows Henry's law, but this law does not apply when xylidine is used. In this case less heat would be generated in the absorber when treating the higher grades of sulfur dioxide with dimethylaniline than with xylidine. This would entail a less efficient cooling system when using dimethylaniline.

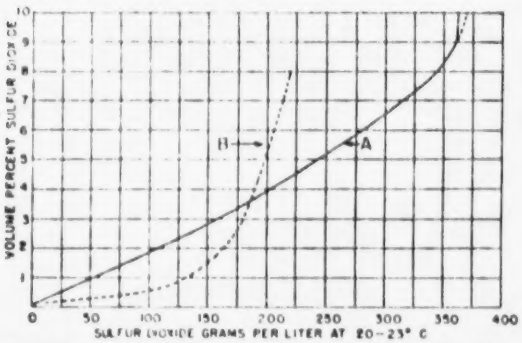

Figure 1. Absorption Isotherms of Sulfur Dioxide

Curve A = sulfur dioxide and anhydrous dimethylaniline; Curve B = sulfur dioxide and xylidine (1:1 xylidine and water)

The vapor pressure of dimethylaniline at 20° C. is 0.35 mm., and the vapor pressure of xylidine at the same temperature is 0.20 mm. This indicates a slight saving of sulfuric acid when recovering xylidine vapor as compared with dimethylaniline vapor.

The solubility of dimethylaniline sulfate in water is much greater than the solubility of xylidine sulfate in water. Therefore the weak sulfuric acid solution from the scrubbers, when using dimethylaniline, can carry a much greater load of dimethylaniline to the regenerator than when xylidine is used. To some extent this greater solubility would offset the advantage of the lower vapor pressure of xylidine.

During the absorption of sulfur dioxide with either dimethylaniline or xylidine there is some oxidation of sulfur dioxide to sulfur trioxide although in the treatment of gas containing 3.5% sulfur dioxide or over, the conversion is quite small, being approximately 0.50%. In the treatment of gas under this grade, the percentage of oxidation increases rapidly, particularly with the use of xylidine in water suspension.

In the dimethylaniline process all the water eliminated as steam from the regenerating and stripping operation is condensed. After removal from the anhydrous dimethylaniline in the gravity separator, all the water phase is returned to the regenerator. Under these conditions the sulfate radical which forms is continuously removed from the absorption circuit thus eliminating the possible formation of any solid reaction products.

With the use of the xylidine-water suspension process, great care must be taken to prevent the formation of solid reaction products, even when treating gas relatively high in sulfur dioxide. In this case, if the sulfate radical in the water phase is not kept within low limits by bleeding sufficient water to the regenerator, rapid autoxidation takes place to the extent that the xylidine sulfate, having a low water solubility, is precipitated and the system becomes clogged.

When treating a low grade sulfur dioxide gas with xylidine, the rate of oxidation to sulfur trioxide is relatively high and a large portion of the water phase must be returned continuously to the regenerator. This must be replaced with fresh water and carefully controlled additions of sodium carbonate to ensure the absence of free acid during absorption. This consumption of soda is in addition to that used in the soda scrubber for the regeneration of xylidine.

The above remarks on the use of xylidine are pertinent because the Asarco process is well adapted for its application in the treatment of low grade sulfur dioxide gas. Xylidine, in this case, has the advantages of greater absorbant capacity and lower vapor pressure over dimethylaniline. However, owing to high water load on regenerator and control of oxidation, dimethylaniline has the advantage of lower steam consumption, and the process requires fewer skilled operators and less supervision. Also, on very low grade gas, soda consumption would probably be in favor of the use of dimethylaniline because of oxidation control when using xylidine.

Just where the use of dimethylaniline would have to give way to xylidine in the matter of operating costs, is not known at present. As far as construction costs are concerned there would be little difference when using the Asarco system of operation. In the opinion of the authors the advantages of dimethylaniline are such that it can be used competitively with xylidine on sulfur dioxide gas as low as 2.0% by volume.

Following 6 months' operation of a 1-ton dimethylaniline absorption unit on 6.0% sulfur dioxide gas at Garfield, Utah, it was decided to build a 2.5-ton unit at Tacoma, Wash. Here, the gas was intermittent and low grade, approximately 3.5% by volume on an average 24-hour basis. For intermittent periods totaling 6 hours, there was no gas coming from copper converters, so this would be a relatively severe test of the commercial possibilities of the process. The plant was put into operation in September 1942 and ran through March 1943. The results from this campaign were better than expected and Asarco decided to build a commercial unit using the Tacoma design as a model.

After considering the relative advantages of Tacoma, Wash., and Selby, Calif., as a site, the latter was selected as it offered better possibilities for commercial return on a lower investment. At Selby the process could be developed to greater advantage as the more profitable, but rather limited, market for sale of sulfur dioxide as a chemical was available.

At present, liquid sulfur dioxide is a chemical of rather minor importance, the total production and consumption in United States being approximately 125 tons per day; of this amount between 15 and 20 tons per day are consumed on the Pacific Coast. The industries using the product are: oil refining, fruit curing, textiles, beet sugar refining, chemical, wine and beer producers, alkaline soil treatment, refrigeration, and use as an antichlor in the purification of water. However, the individual consumption of all these industries is relatively small.

Prior to the erection of the Selby plant, all United States production was made by the use of the Haenisch-Schroeder water-absorption process operating on burner gas derived from brimstone. There were eight small plants of this type and because of high transportation costs they were geographically distributed to satisfy the local markets. With limited markets, there was little incentive for producers to install new plants that could take advantage of better absorbants and modern chemical engineering practice. Such plants are relatively expensive to build, and because of the high market price of the product, existing plants made good money in spite of high operating costs. At present the market price for technical grade sulfur dioxide ranges from $70 to $90 per ton in tank carlots, f.o.b. plant.

Although all the plants in this country absorbed the sulfur dioxide in water, a combination of severe restrictions on emission of smelter smoke and relatively high cost of brimstone had forced Europeans into the use of efficient absorbants that would function on their low grade smelter gases. By 1940 three small "sulphidine" plants had been installed in Germany, Belgium, and France; one Imperial Chemical plant using basic aluminum sulfate was operating at Imatra, Finland, and Falconbridge Nickel Company, in cooperation with the firm of Guggenheim Brothers, had installed at Kristiansand, Norway, a small plant using anhydrous dimethylaniline. The use of dimethylaniline was investigated by Asarco in cooperation with the Guggenheim firm at the

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time of the Norwegian installation, but Asarco took no part in the design of plant, and the operation there did not follow the present process system as installed at Selby. Recently, changes have been made at Kristiansand to take advantage of some features of the Asarco process.

The present plant at the Selby lead smelter went into operation in September 1947. In order to take care of the bulk of Pacific Coast requirements and allow a surplus of 100% sulfur dioxide gas for enriching and stabilizing the supply to adjoining acid plant, the design called for a capacity of 20 tons per day. This was based on a supply of gas from Dwight-Lloyd sintering machines averaging 5.0% sulfur dioxide by volume. As regards plant capacity, steam consumption, dimethylaniline loss, and quality of operation the unit has exceeded expectations.

Operations during 1949 indicate the following basic data:

Recovery of SO_2 from 5.0% gas, %	99.0
Dimethylaniline consumed, ton SO_2 produced, lb.	1.1
Sodium carbonate consumed, ton SO_2 produced, lb.	35.0
Sulfuric acid consumed, ton SO_2 produced, lb.	40.0
Steam consumed/ton SO_2 produced, tons	1.2
Power*, kw.-hr.	145
Cooling water at 65° F., gal./min	300

* Provided the SO_2 is produced as a 100% gas, power consumption will be approximately 100 kw.-hr.

These data do not include labor, power, and water used for the purification of gas prior to entering the sulfur dioxide plant proper.

The labor required to operate the plant consists of one foreman on day shift only, three shift operators, and one general utility man on day shift. The same crew can operate a plant of several times Selby's capacity. In addition, supervision and some chemical control work are required.

It is difficult at this time to give a fair estimate of maintenance costs. The plant has been going through a development stage in the selection of the best corrosion resistant material. Recently, lead has been substituted for 316 stainless steel in the construction of heat exchangers and solution coolers with marked success, and until the benefits of this and other improvements are realized, it would be misleading to set a definite figure on this cost. The Selby unit is also, to some extent, handicapped by the use of salt water for cooling.

The matter of gas purification has been given no consideration in the above discussion. In general this will follow the same lines as purification for production of contact sulfuric acid, although for sulfur dioxide, purification does not require the same high degree of efficiency. Gas purification generally consists of:

1. Hot Cottrell for the removal of dust and fume
2. Water scrubber for removal of residual fume and cooling and conditioning gas for further Cottrell treatment
3. Mist Cottrell for removal of physical water and sulfuric acid mist
4. Small coke filter for removal of last traces of physical water

A diagrammatic sketch of the Selby gas cleaning is shown in Figure 2. The elaborate gas purification system at Selby is necessary because of the high impurities in the gas stream.

ASARCO SULFUR DIOXIDE PROCESS

The process for the recovery of sulfur dioxide from flue gas by means of dimethylaniline absorbant, as developed by the American Smelting and Refining Company, consists essentially of two related closed circuit operations, carried out simultaneously, in the two main bubble-cap towers—namely, the absorbing tower and the stripping tower. The first operation consists of recovery of sulfur dioxide from the flue gas by absorption in dimethylaniline and its subsequent stripping from the pregnant dimethylaniline. The second operation consists of the recovery of the dimethylaniline which escapes into the gas stream during the absorption operation and from that dissolved in water during the stripping operation. Without the recovery of dimethylaniline the process would not be economical. In each of the two bubble-cap towers more than one operation is carried out at the same time. This is shown on the flow sheet, Figure 3.

The absorption tower consists of a single bubble-plate column divided into three separate units. The bottom, or first unit, consists of eight bubble-cap trays where the absorption of sulfur dioxide takes place. The second unit of two bubble-cap trays, directly above the first unit, serves to convert sodium carbonate to sodium sulfite or bisulfite. The third, or top unit, consists of nine bubble cap trays and serves to absorb and recover the dimethylaniline from the flue gas stream. Each unit in the absorbing tower is separate and distinct in operation and is provided with independent inlet and outlet nozzles for the liquid flow. The liquid phases of the three units are kept separate for subsequent treatment.

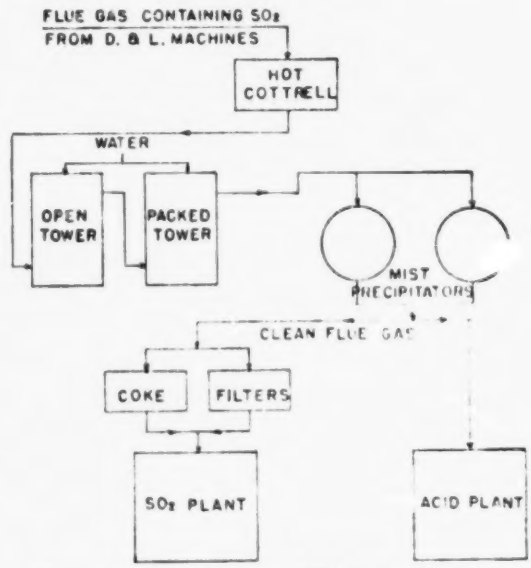

Figure 2. Flow Diagram of Selby Gas Cleaning System

The stripping tower consists, also, of a single bubble-plate column and is divided into three units. The bottom or first unit, the regenerator, consists of seven bubble-cap trays and serves to regenerate the dimethylaniline which was captured in the top unit of the absorbing tower. The second or middle unit of fourteen bubble-cap trays is where the sulfur dioxide is liberated from the pregnant dimethylaniline. This is called the stripper. The top unit, consisting of five trays of bubble caps, is used to recover the dimethylaniline vapor from the strong sulfur dioxide which was liberated from the stripper.

RECOVERY OF SULFUR DIOXIDE

Clean flue gas is forced by the blower, Figure 3, through the gas cooler, where the temperature of the gas is reduced, into the bottom of the absorber where it flows upward through the tower. The flue gas bubbles through a descending current of cool anhydrous dimethylaniline which flows downward from tray to tray following admission to the absorber through metering devices from the supply in the dimethylaniline surge tank. The sulfur dioxide dissolves in the dimethylaniline, and as the flue gas becomes impoverished in sulfur dioxide it becomes enriched with dimethylaniline vapor. The dimethylaniline in flowing downward from tray to tray becomes richer in dissolved sulfur dioxide and changes in color from light yellow to red as the saturated solution.

Considerable heat is evolved during the absorption of sulfur dioxide by the dimethylaniline, and intercoolers and pumps are

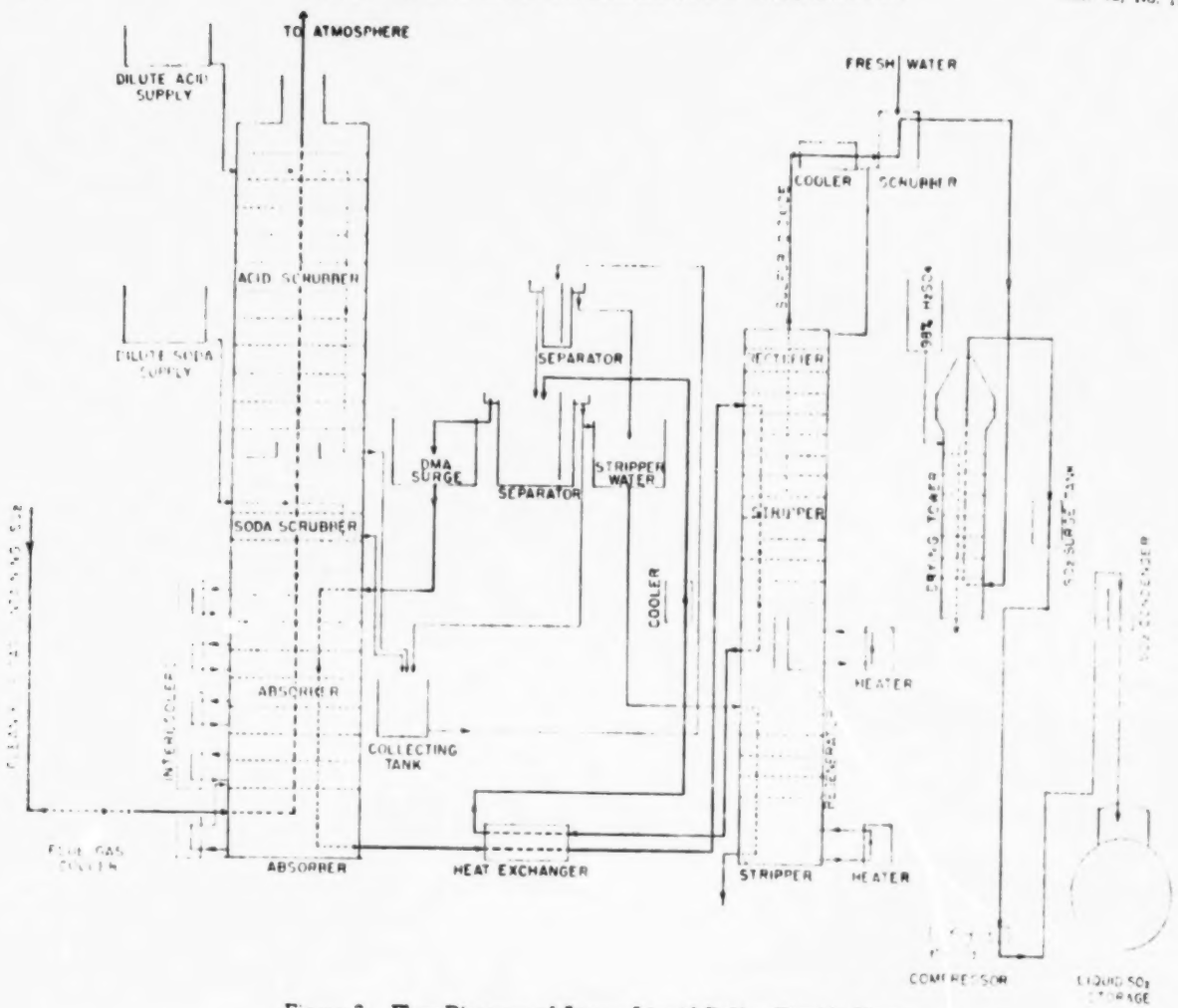

Figure 3. Flow Diagram of Asarco Liquid Sulfur Dioxide Plant

provided on the absorber to dissipate this heat of solution. The quantity of sulfur dioxide which a given weight of dimethylaniline can dissolve is a function of the temperature of the absorbing liquid and the concentration of sulfur dioxide in the flue gas, the pressure being constant at about 30 inches of water (Figure 1, curve A). Lowering the temperature of the absorbant accomplishes two important things: (1) increases the capacity of a unit of dimethylaniline to transfer sulfur dioxide and (2) reduces the vapor pressure of the dimethylaniline, thus saving reagents for the subsequent recovery of the dimethylaniline absorbant.

The transfer of sulfur dioxide by the dimethylaniline off the bottom tray of the absorber is about 60% of the equilibrium value as shown in curve *A*, with a tail gas of less than 0.10% sulfur dioxide.

The pregnant dimethylaniline is discharged from the absorber through a liquid-level control valve and is pumped through the heat exchanger in heat exchange relationship to the hot stripped dimethylaniline from the stripper. The heated pregnant dimethylaniline is poured onto the top tray of the stripper unit of the stripping tower, and flows downward from tray to tray, countercurrent to a rising column of steam and sulfur dioxide vapor. The sulfur dioxide is stripped from the dimethylaniline and escapes upward through the tower. The stripped dimethylaniline and condensed steam are discharged from the bottom of the stripper through a liquid-level control valve, are cooled by heat exchange relationship in the heat exchanger, further cooled by a helical coil lead cooler, and pumped into the gravity separator where separation between dimethylaniline and water takes place. The absorbant flows into the dimethylaniline surge tank where it is ready for another cycle. The separated water phase empties into the stripper water tank for subsequent recovery of dissolved dimethylaniline.

The hot sulfur dioxide which was liberated in the stripper flows upward into the rectifier where it is bubbled through water. The water in the presence of sulfur dioxide fixes the dimethylaniline vapor as dimethylaniline sulfite. The dimethylaniline sulfite dissolved in the water overflows into the stripper. The sulfur dioxide gas, substantially free from dimethylaniline vapor, leaves the stripping tower by the exit pipe and is cooled within a few degrees of the temperature of cooling water and scrubbed with cold water to completely remove any residual dimethylaniline vapor. The cold pure sulfur dioxide gas is dried in a bubble-cap tower, which is irrigated with 98% sulfuric acid, then is compressed, cooled, liquefied, and run to storage. The sulfur dioxide at this point contains no dimethylaniline and less than 50 p.p.m. water.

RECOVERY OF DIMETHYLANILINE

The recovery of dimethylaniline vapor from the flue gas stream takes place in the second and third units of the absorbing tower and in the bottom unit of the stripping tower.

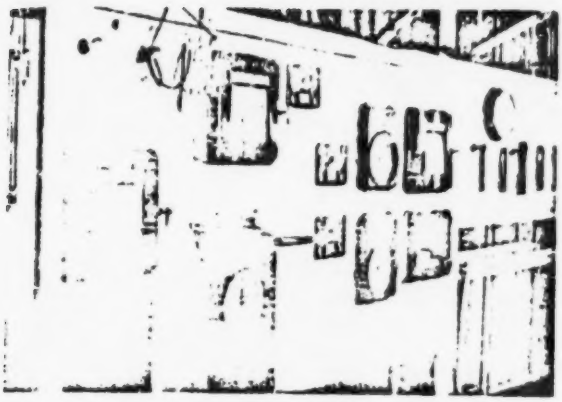

Figure 4. Instrument Panel, Selby Liquid Sulfur Dioxide Plant

The flue gas is impoverished in sulfur dioxide and enriched in dimethylaniline vapors while passing through the absorber unit. The flue gas leaves the absorber and is bubbled through two trays of dilute sodium carbonate solution in the soda scrubber. Any residual sulfur dioxide in the flue gas converts the sodium carbonate to sodium sulfite or bisulfite. The carbon dioxide is liberated in the flue gas. Any spray or droplets of dimethylaniline are trapped in this section and escape with the liquid effluent from this unit.

The flue gas substantially free of physical dimethylaniline liquid but containing vapor of dimethylaniline is caused to bubble through nine trays of bubble caps irrigated with a dilute sulfuric acid solution. The acid and the dimethylaniline base react to form dimethylaniline sulfate.

The dilute sulfuric acid is fed onto the top tray of the third unit of the absorbing tower or the acid scrubber at a rate to almost saturate the acid with dimethylaniline on the bottom tray of this unit and to maintain a concentration of dimethylaniline in the acid scrubber from the top tray of less than one twentieth saturation. The flue gas which leaves the tower at this point and flows into the atmosphere contains a fraction of 1% of sulfur dioxide and practically no dimethylaniline.

The effluent from the soda trays and the acid scrubber empties into a collecting tank and is pumped up to a small gravity separator, where a separation is made between dimethylaniline and water. The dimethylaniline is liberated as a result of the reaction between the dimethylaniline sulfate from the acid scrubber and the sodium sulfite from the soda trays. Part of the dimethylaniline remains dissolved in the water as dimethylaniline sulfite. The dimethylaniline which separates empties into the main dimethylaniline supply. The water empties into the stripper water tank.

The water emptying into the stripper water tank consists of the total water and solution added to the process. This consists of:

1. The dilute sulfuric acid fed to the acid scrubber
2. The dilute sodium carbonate solution fed to the soda scrubber
3. The cold water used to scrub the dimethylaniline from the 100% sulfur dioxide
4. The water condensed from the stripper and pumped into the main separating tank

The water phase, which has been collected in the stripper water tank, is fed onto the top tray of the regenerator. Heat is supplied to the regenerator by steam in the regenerator heater. The liquid on the regenerator trays is boiled vigorously and dimethylaniline is steam distilled into the stripper. Any dimethylaniline sulfite which may have been dissolved in the water is broken down into dimethylaniline base and sulfur dioxide and escapes with the steam into the stripper. The steam and dimethylaniline are condensed in the stripper giving up heat to aid in the stripping of pregnant dimethylaniline. At the temperature of the regenerator the reaction products between dimethylaniline sulfate and sodium sulfite are broken down into free dimethylaniline and sulfur dioxide; the sodium sulfate remains in solution.

The effluent from the regenerator, which consists of the first three items listed above, is discharged through a float valve to a pH cell and then to the sewer. The sodium sulfate formed in the regenerator is thrown to waste.

The pH of the water solution in the regenerator is maintained between 5 and 6 and is adjusted by the rate of flow of sodium carbonate solution to the soda scrubber. The effluent water contains no dissolved dimethylaniline.

There are only three possible sources of loss of dimethylaniline from the process cycle—namely:

1. As dimethylaniline vapor escaping from the absorption tower with the impoverished flue gas
2. As dimethylaniline dissolved in the water effluent from the regenerator
3. As mechanical leaks in pump glands, valve packing glands, and pipe threads

The first two sources of loss are recoverable and may be controlled by correct operation of the process, and the third source of loss is preventable.

The operation of the Asarco process is smooth and flexible. The plant may be shut down and started up without difficulty. There are only six control valves on the process; these control solution flow rates, and the levels of liquid in the various units are automatically maintained by float valves. There is no juggling of flow rates to maintain normal liquid levels in the units in the two bubble-cap towers.

The operation of the plant takes place principally from one

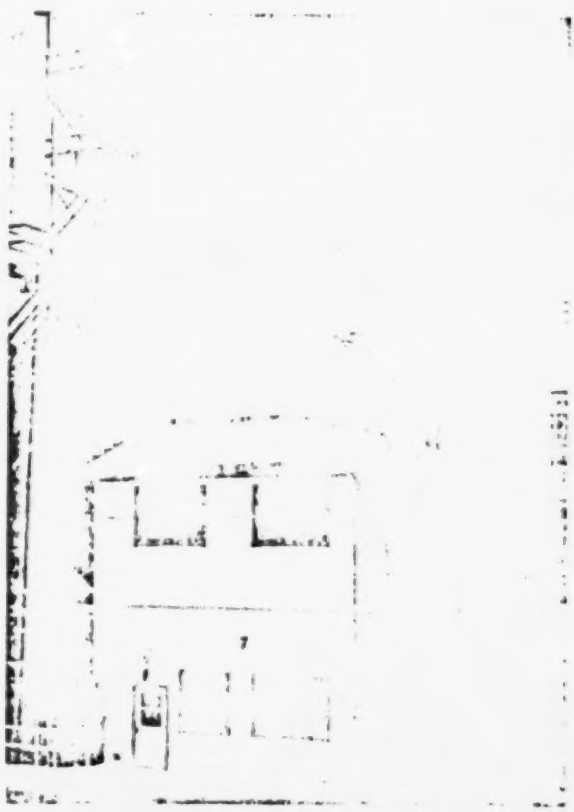

Figure 5. Selby Liquid Sulfur Dioxide Plant

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floor and from one instrument panel. This is shown in Figure 4. The instruments consist of a temperature recorder, a vacuum and pressure gage for blower and absorber, integrating and recording flue gas flowmeter and steam flowmeter, rotameter for liquid flow control, and remote indicating tank level gages. The instruments also included two specially designed sulfur dioxide recorders, one for the head gas and one for the tail gas. This instrument was designed by Thomas, Ivie, and Fitt, of the American Smelting and Refining Company (*8*). These instruments record sulfur dioxide in the presence of carbon dioxide accurately and since the sinter gas at Selby contains a few per cent of carbon dioxide, the analysis of the gas for sulfur dioxide alone is important. Furthermore, the tail gas recorder records minute amounts of sulfur dioxide, and since the tail gas is in the range 0.05 to 0.06% sulfur dioxide this instrument is important for plant operation.

At present three plants are operating producing sulfur dioxide by using anhydrous dimethylaniline: one is the Falconbridge Nickel Company at Kristiansand, Norway; the second is the Selby unit of the American Smelting and Refining Company at Selby, Calif. (Figure 5); and the third, which went into operation a few months ago, is a duplicate of the Selby unit, built by the Tennessee Copper Company, Copperhill, Tenn., under license from Asarco. Several other plants of greater capacity are under consideration.

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Recovery of Sulfur Compounds from Atmospheric Contaminants

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The emission of sulfur compounds, recognized as major atmospheric contaminants, must be reduced as a matter of economics and in the interest of public welfare. Great strides have been made in the control of smelter smoke damage by scientific investigation of sulfur dioxide injury to plant life, and the application of remedial measures, which include use of high stacks and high temperatures for the discharge of waste gases, continuous automatic measurement of ground concentrations and application of meteorological control by accurate forecasting of critical weather conditions, and installation of recovery plants for conversion of excess sulfur dioxide to liquid sulfur dioxide, sulfuric acid, fertilizers, or elemental sulfur. The annual losses of sulfur from products discharged to the atmosphere from zinc plants, lead, copper, and nickel smelters, crude oil refineries, and from coal combustion, are compared with world native sulfur production and by-product sulfur recovery. The extent to which sulfur emission must be reduced, to avoid injury to plant life, is discussed in terms of the permissible levels of ground concentration. Methods for recovery of sulfur compounds from sulfur dioxide and hydrogen sulfide in stack gas include concentration of sulfur dioxide and its conversion to sulfuric acid, recovery as elemental sulfur, and flue gas disposal of the effluent and noneffluent types. New developments of outstanding importance for purification and recovery of sulfur dioxide are embodied in the Trail ammonia process, the dimethylaniline process at Selby, and flash smelting at Copper Cliff in conjunction with liquid sulfur dioxide recovery. An aroused public consciousness of the need of controlling atmospheric pollution has stimulated investigation in many contaminated areas. Sulfur contaminants may be profitably recovered in many industrial operations and thus clean up the air and add to native sulfur reserves, which are rapidly being depleted in the United States. More research is needed in industries confronted with difficult recovery problems—for example, nickel smelters. Cooperation between major native sulfur producers and companies with a large sulfur problem on their hands is desirable.

SULFUR compounds have been recognized as major atmospheric contaminants for many years in the metal smelting and oil refining industries, and in all operations involving the consumption of large quantities of sulfur-containing fuels such as coal. Enormous damage has been caused by the excessive emission and wastage of such products to agricultural and forest areas, and to materials such as metals, stone, cement, paint, paper, leather, and textiles. The annual losses from air pollution cannot be assessed accurately but, nevertheless, amount to many millions of dollars. If one considers that a substantial portion of the sulfur dioxide or hydrogen sulfide lost to the atmosphere may be economically recovered, the real magnitude of such losses and the importance of this problem become apparent.

Within the past 20 years a great scientific effort has been made in the United States, Canada, and elsewhere to determine the causes of air pollution and to develop technical methods of control. The effect of sulfur dioxide on plant life and metabolism, photosynthesis and respiration, and the factors affecting susceptibility have been evaluated with scientific accuracy. Considerable insight has been gained into the role of micrometeorology and the influence of topography on smog conditions accom-